Direct Observation of a Nuclear Spin Excitation in $Ho_2Ti_2O_7$

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A single nondispersive excitation is observed by means of neutron backscattering, at $E_0 = 26.3$ μeV in the spin ice $Ho_2Ti_2O_7$ but not in the isotopically enriched $^{162}Dy_2Ti_2O_7$ analogue. The intensity of this excitation is rather small, $\lesssim 0.2\%$ of the elastic intensity. It is clearly observed below 80 K but resolution limited only below $\sim$65 K. The application of a magnetic field up to $\mu_0 H = 4.5$ T, at 1.6 K, has no measurable effect on the energy or intensity. This nuclear excitation is believed to perturb the electronic, Ising spin system resulting in the persistent spin dynamics observed in spin ice compounds.

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Understanding the nature of electronic and nuclear spins of a system and how they can be manipulated is essential if spintronic devices and quantum computers are to benefit society in the same way semiconductors have done until now [1]. Indeed, one can imagine a nuclear spin, solid-state device where information is stored in the nucleus and manipulated through the electronic spin system [2,3]. The interaction Hamiltonian for two spin systems [through the hyperfine (hf) field] is usually written in the form

$$\mathcal{H} = A(\boldsymbol{I} \cdot \boldsymbol{J}),$$

where A is a constant in the low $\sim\mu$eV range and $\boldsymbol{I}$, $\boldsymbol{J}$ are the nuclear and electronic spin operators, respectively.

Schermer and Blume [4] were the first to calculate the differential neutron scattering cross section for a nuclear spin ensemble, showing that one can use the power of this technique to probe nuclear excitations. Besides an isotope with a nuclear spin and a large incoherent scattering cross section, a spectrometer with very high energy resolution is required to observe the associated excitations, because these are usually within 10^0 μeV. Low temperatures, $T \lesssim 1$ K, are typically required to suppress any dynamics of the electronic spin system which will normally dominate the inelastic neutron scattering signal. Although many compounds would satisfy the criteria laid out above, one also needs a large hyperfine field at the nucleus. Most recent neutron studies of nuclear spin excitations have been performed in electronically ordered Nd compounds, where the ^{143}Nd and ^{145}Nd isotopes have a large nuclear spin ($I = 7/2$), and where the incoherent scattering cross section and the hf field are relatively large [5,6]. Holmium compounds are also good candidates for nuclear spin studies, since holmium has only one stable isotope, ^{165}Ho, with a nuclear spin $I = 7/2$ and a large magnetic dipole moment of $+4.17\mu_N$ [7].

A good Ho-based candidate for such a study is $Ho_2Ti_2O_7$, where unusually sluggish low temperature spin dynamics have been observed [8–13]. It has been suggested that residual fluctuations seen below 2 K are a consequence of the nuclear spins perturbing the electronic spins off their $\langle 111 \rangle$ equilibrium axes. $Ho_2Ti_2O_7$ (HoTO) and $Dy_2Ti_2O_7$ (DyTO) are spin ices [14–30] whose spin dynamics have been investigated over the past 10 years. In the paramagnetic, or liquidlike, high temperature phase a thermally activated, Arrhenius process dominates the magnetic spectrum. As the temperature is lowered below 30 K, both compounds enter a quantum regime where temperature plays no role in the spin relaxation processes [10,11]. The electronic spin fluctuations here are a result of spin tunneling between degenerate $|\pm M_J\rangle$ states. They may also be regarded as local ''zero energy'' modes giving rise to a strong, quasielastic signal in neutron scattering with a Q-independent width. Below 1 K, a thermally activated process is seen to regain dominance in both HoTO and DyTO. This reentrant behavior from quantum to thermally activated as the temperature is lowered appears to be unique to the spin ices. Neutron spin echo experiments have probed all three states in spin ice [10,12,31,32] and revealed a small fraction of the spin system ($<3\%$) in HoTO that remains dynamic at 300 mK. These different dynamical regimes and the persistent spin dynamics have also been studied in both spin ices by ac susceptibility and muon spin relaxation [25–28].

In this Letter we report, for the first time, a nuclear spin excitation in HoTO and some quaternary derivatives. The observation of an associated nondispersive mode at $E_0 = 26.3$ μeV over an unusually wide temperature range, $T \lesssim 100$ K, opens the opportunity to study how the two spin systems interact with each other.

Samples of $Ho_2Ti_2O_7$, $Ho_{1.6}La_{0.4}Ti_2O_7$ (HoLaTO), and $Ho_{0.7}Y_{1.3}Ti_2O_7$ (HoYTO) were prepared by the usual solid state reaction from oxide starting materials. The cubic pyrochlore structure shown in Fig. 1 was confirmed by x-ray diffraction. Natural dysprosium has two isotopes with large

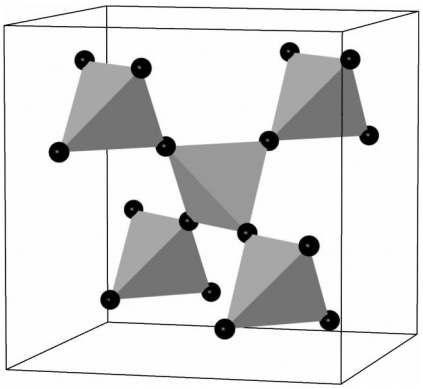

FIG. 1. The rare-earth sublattice of corner-sharing tetrahedra in the pyrochlore structure adopted by the spin ices.

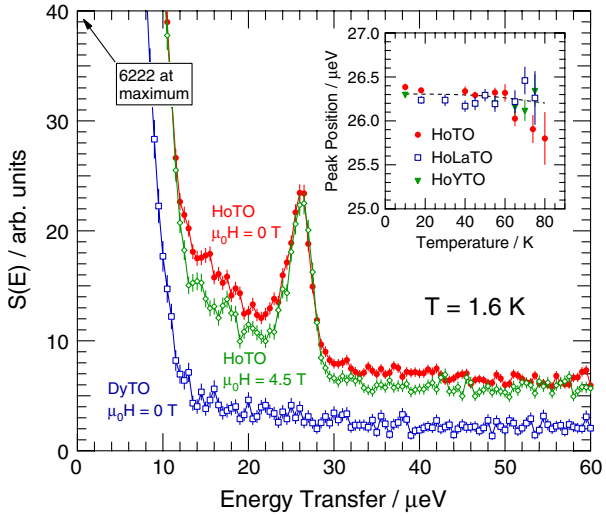

FIG. 2 (color online). Integrated scattering function $S(E)$ comparing $Ho_2Ti_2O_7$ (●), $^{162}Dy_2Ti_2O_7$ (□), and $Ho_2Ti_2O_7$ in 4.5 T (◇) showing a single inelastic excitation. The inset shows the temperature dependence of the peak position for all three Ho samples: $Ho_2Ti_2O_7$ (●), $Ho_{1.6}La_{0.4}Ti_2O_7$ (□), and $Ho_{0.7}Y_{1.3}Ti_2O_7$ (▼), with a possible slight softening towards high temperature (the line is a guide to the eye).

absorption cross sections for cold neutrons, ^{161}Dy and ^{164}Dy. Therefore enriched $^{162}Dy_2O_3$ oxide was used in the preparation of a 950 mg ^{162}DyTO sample. In the series of experiments reported here we have utilized the new backscattering spectrometer BASIS at beam line 2 at the Spallation Neutron Source (SNS) in Oak Ridge [33,34]. This instrument offers a high energy resolution, ~3.3 μeV full width at half maximum with our particular sample size, and a superior signal-to-noise ratio. In one experiment, a cryomagnet was used with a maximum field of $\mu_0 H = 5$ T and a base temperature of $T = 1.6$ K. The powders were very tightly packed in their containers to avoid reorientation of the grains in a magnetic field. In other experiments, a closed cycle refrigerator was used to cool the sample down to 7 K.

As shown in Fig. 2, we observe the excitation in HoTO in zero field and at $\mu_0 H = 4.5$ T. Clearly, the peak is insensitive to magnetic field: A measurement at $\mu_0 H = 2$ T gave the same result (not shown). The figure also shows the absence of a comparable excitation in ^{162}DyTO at the same temperature in zero applied field. The excitation is resolution limited below ~65 K and no other inelastic feature was observable out to ± 1100 μeV, consistent with earlier studies [10,28]. The data in the figure are normalized to proton charge on target (i.e., source intensity) and corrected with a neutron monitor intensity to account for the incident wavelength-dependent spectrum. The data are also integrated over the available Q range as there is no apparent Q dependence to the energy, width, or intensity of the excitation. The signal from ^{162}DyTO is overall much lower because of the small sample size. As shown in the inset of Fig. 2, the energy transfer is the same for all three Ho compounds studied (within experimental error due to counting statistics, ~0.05 μeV) and apart from a possible softening at the highest temperatures, constant below 80 K.

The complete lack of field dependence to the excitation is of particular interest. Below 2 K in zero field the sample is in the spin ice state, a disordered magnet with short ranged dynamic spin correlations that obey the two-in, two-out ice rules [8]. In a field, at these temperatures the system enters a long range ordered state [14,15,29], which is directly confirmed in our data by the presence of magnetic Bragg peaks. In this state, plateaus are seen in magnetization curves [22–24], and the short ranged dynamic correlations are largely suppressed. This confirms that the zero field data were taken in the spin ice state, and suggests that the excitation does not originate from within the electronic spins.

The scattering function $S(E)$ is displayed for the HoLaTO system in Fig. 3 over a larger energy range. The defining feature is the large quasielastic intensity from electronic spin fluctuations, but the small excitation at E_0 can be seen in the 10 K data set. Note that, if the intensity of the excitation was independent of temperature, it would still be seen at 100 K even though the quasielastic intensity is much stronger. The temperature dependence of the scattering intensity of the excitation is shown in the inset and is very similar if not identical for the three Ho systems studied. In an attempt to determine how the intensity scales with the Ho concentration, a scale factor was calculated for each sample as the quotient of the measured (111) Bragg intensity and the square of the (111) powder averaged structure factor [35]. The nuclear (111) Bragg intensity provides a convenient internal calibration for the exact sample mass in the beam and the neutron beam attenuation which depends on the stoichiometric composition and the powder packing factor. As can be seen in the inset of Fig. 3, between the three samples the normalized intensity varies like

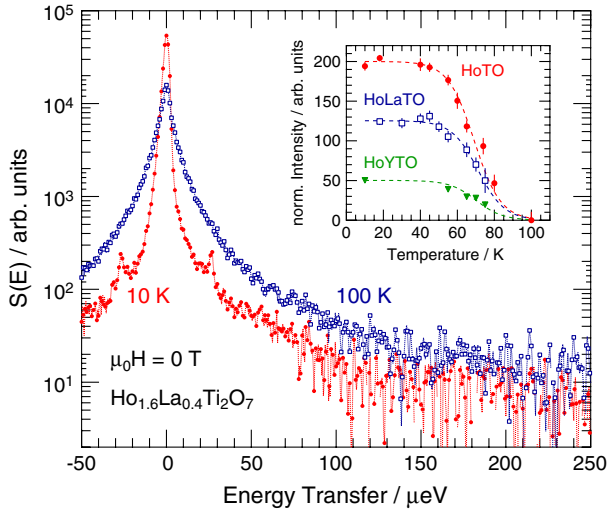

FIG. 3 (color online). Integrated $S(E)$ of $Ho_{1.6}La_{0.4}Ti_2O_7$ at temperatures of 10 and 100 K in zero field, showing the dominance of the central quasielastic line (main figure) due to electronic spin flips. The inset shows the temperature dependence of the inelastic excitation for the three Ho samples: $Ho_2Ti_2O_7$ (●), $Ho_{1.6}La_{0.4}Ti_2O_7$ (□), and $Ho_{0.7}Y_{1.3}Ti_2O_7$ (▼). The lines are guides to the eye.

$$2.00 : (1.28 \pm 0.08) : (0.53 \pm 0.03),$$

where the error bars arise from counting statistics, which approximately scales with the Ho contents of the three samples,

$$2.00 : 1.60 : 0.70.$$

The most likely origin of this excitation is a transition between nuclear Ho spin states split in the hf field. The most significant support for this claim is from consistent specific heat data, while the absence of a similar excitation in our ^{162}DyTO sample, the lack of a dependence on scattering vector Q or magnetic field (up to ~5 T), and the approximate scaling with the number of Ho ions in a sample are considered as supporting evidence.

The low temperature heat capacity of HoTO and Ho_2GaSbO_7 are very similar with a large hf contribution peaked at 0.3 K [19,36]. This has been related to a Schottky anomaly for nuclear Ho spin ($I = 7/2$) of $0.9R$, and the level splitting of 0.3 K equals ~26 μeV. The hf field at the Ho nucleus corresponding to the splitting amounts to $B_{\mathrm{hf}} = (7/2)E_0/\mu_{\mathrm{Ho}} = (702 \pm 1)$ T, a value that matches a previous estimate, $B_{\mathrm{hf}} \sim 720$ T [37], and is comparable to pure Ho metal (770 T) [38]. This provides an explanation for the lack of a field dependence to the excitation: An applied external field of 5 T will not add significantly to a hf field at this magnitude.

Dysprosium has five stable isotopes, but only ^{161}Dy and ^{163}Dy have nuclear dipole moments ($-0.48\mu_N$ and $+0.67\mu_N$, respectively) [39]. The smaller moment and the dilution of the nuclear spin system in DyTO result in a nuclear contribution to the heat capacity peaked at 20 mK, rather than the 300 mK seen in HoTO. However, an upper limit of only 0.6% of the Dy nuclei in our enriched sample can have a spin, and thus no nuclear excitations are expected.

We now discuss the temperature dependence of the energy and the intensity of the excitation. It is known that the hf field produced by the orbital angular momentum of the $4f$ electrons is proportional to the magnetic moment of the ion [6,38]. The temperature dependence of the moment $J(J+1)$ of HoTO has been measured up to $T \sim 800$ K [12]. At intermediate Q, $Q \sim 1.5$ Å^{-1}, where correlation effects are small and the magnetic scattered intensity is a good measure of the moment, the intensity is constant below ~60 K, and drops only slightly towards 100 K. The observed nearly constant excitation energy is therefore consistent with this result, as the magnitude of the hf field is expected to show little temperature dependence. The excitation starts weakening noticeably above $T \sim 50$ K and vanishes above $T \sim 90$ K. This is reflecting the *dynamics* of the hf field which fluctuates at the same rate as the ensemble of the electronic spins. In this temperature range, between 50 and 100 K, the temperature dependent fluctuation rate follows an Arrhenius law, $\nu = \nu_0 \exp(-\Delta/T)$, with $\nu_0 = 1.1 \times 10^{11}$ Hz and $\Delta = 293$ K [12]. The relevant quantity to compare to is the Larmor frequency of the Ho nuclear moment in the hf field, which is estimated at $\nu_L \sim 6.36$ GHz (with the gyromagnetic ratio of the Ho nucleus equal to $\gamma/2\pi = 9.06$ MHz/T). Inputting this value in the Arrhenius relation above, this is the fluctuation rate of the hf field at $T_L \sim 103$ K. At low temperature, $T \ll T_L$, the hf field appears static and the transitions between nuclear states can be observed. At higher temperature, when the hf field fluctuates at a rate comparable to ν_L or faster, this is no longer the case as the nuclei experience a time averaged hf field. The excitation is thus expected to vanish around T_L, consistent with the observation.

Considering the scattering intensity, it also appears plausible that the excitation is due to the nuclear spin of the Ho ions. It is clear that it is associated with either the electronic or nuclear spin system of the Ho ion because the intensity scales well with the Ho concentration. With the unit magnetic scattering length $r_0 = -0.54 \times 10^{-12}$ cm, an ion with a localized electronic moment of $\sim 10\mu_B$ will attain a magnetic scattering cross section $\sim 4\pi(10r_0)^2 = 370$ b. Neglecting coherence effects and a structure factor, this may be compared to the incoherent scattering cross section of Ho (which is entirely spin incoherent since there is only one isotope) of 0.36 b, which is ~1000 times smaller. Figure 3 shows that the intensity of the excitation is indeed about 500 times smaller than the quasielastic intensity.

Summing up all the above arguments for a nuclear origin of the excitation, the possibility that it does in fact originate from the electronic spin system appears very unlikely as

we now discuss. An energy scale of 0.3 K is associated with the electronic moments in spin ice in a couple of ways. First, the energy gained by a spin flip within the disordered, dipolar spin ice state (below 2 K), moving towards an ordered state proposed by the dipolar spin ice model, is ≈ 0.2 K [20,21]. However, since this ordered state has not been experimentally observed at 50 mK, the energy scale must be significantly lower and it is therefore unlikely to be what we have observed. More recently, it has been proposed that magnetic monopoles can propagate through the magnetic spin ice lattice [30]. The authors calculate that once the separation between monopoles is large, the cost of increasing the length of the ''Dirac string'' is approximately 0.3 K per unit. Associating the observed excitation to the electronic spin system is problematic because it is not seen in ^{162}DyTO and moreover it is surprisingly robust in magnetic fields.

What implications does this result have for spin ice and frustration physics? If due to the nuclear moments, one can expect that the excitation persists to near zero temperature. As was proposed by Waugh and Slichter [40], such dynamics can couple to the electronic spins causing them to ''wobble,'' resulting in persistent spin dynamics. Experimental evidence for this in HoTO comes from neutron spin echo [10] and zero field muon spin relaxation (μSR) [27] results, and a similar claim has been made for the DyTO system from longitudinal field μSR [28]. Such a scenario would mostly apply for HoTO but also (to a smaller extent because the nuclear moments are 10 times smaller) to DyTO with natural Dy that contains the ^{161}Dy and ^{163}Dy isotopes. Indeed, unlike HoTO, the DyTO muon results show a $1/3$ recovery of the signal indicative of a more static system. A very interesting experimental test would be to perform a comparative study of DyTO and ^{162}DyTO with a technique that can detect persistent spin dynamics.

To conclude, we have observed a low energy excitation in several Ho-based spin ice systems. From the energy scale associated with this excitation, and its dependence on temperature, holmium concentration and applied magnetic field, we have identified it as an excitation between nuclear spin states which have been split by a large hyperfine field known to be present in the spin ice compounds. The lack of a similar excitation in $^{162}Dy_2Ti_2O_7$ with no nuclear spin helps to reinforce this conclusion.

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